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**Design, production and characterisation of granular adsorbent material for
arsenic removal from contaminated wastewater**

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ABSTRACT

The objective of this research was to design granulated iron oxide for the adsorption of heavy metals from wastewater. Polyvinyl acetate (PVAc) was chosen as a suitable binder; as it is water insoluble. Initial experiments on selection of suitable solvent of the polymer were carried out using three solvents namely; methanol, acetone and toluene. Based on the initial tests on product yield and mechanical strength, acetone was selected as the solvent for the polyvinyl acetate binder. Design of experiment was then used to investigate the influence of granulation process variables; impeller speed, binder concentration and liquid to solid ratio on the properties of the granular materials. The response variables in the study were granules mean size, stability in water and granule strength. The results showed that the combination of high impeller speed and high binder concentration favour the formation of strong and stable granules. Results also showed that leaching of the binder into the simulated wastewater was negligible. Trial adsorption experiments carried out using the strongest and most stable iron oxide granules produced in this work showed removal efficiency of around 70% of synthetic arsenic solutions with initial concentration of 1000 ppb.

KEYWORDS: stability coefficient, adsorbent granules, arsenic removal, high shear granulation

1. INTRODUCTION

Due to lower operation costs and high removal efficiencies, the use of adsorption technology for specific removal of contaminants such as fluorides and heavy metals from ground water and wastewater, has recently increased in comparison with other technologies such as reverse osmosis, nano-filtration and electro-dialysis (Albadarin et al., 2014b; Albadarin et al., 2014c; Mostafa et al., 2011; Zhao et al., 2012). The adsorption technique is capable of removing different species of contaminants over a wide range of concentration and pH values by utilising different types of materials as adsorbents (Albadarin et al., 2014a; Albadarin et al., 2012; Albadarin et al., 2014b; Cope et al., 2014; Glocheux et al., 2014; Glocheux et al., 2015; Hai-Xia Wu 2011; Lunge et al., 2014; Mangwandi et al., 2011b; Mangwandi et al., 2014; Yürüm et al., 2014). A wide range of materials such as inorganic metal oxides and hydroxides (Albadarin et al., 2014b; Albadarin et al., 2014c; Glocheux et al., 2014; Halim et al., 2008), natural materials (Albadarin et al., 2014b; Halim et al., 2008; Mangwandi et al., 2013a), novel materials (Albadarin et al., 2014c; Glocheux et al., 2014; Hai-Xia Wu 2011; Mangwandi et al., 2013a; Zhao et al., 2012), activated carbons and minerals have been used as adsorbent materials for removal of various pollutants from wastewater.

The most commonly used adsorbents are activated alumina and activated carbon (Hai-Xia Wu 2011; Mostafa et al., 2011). However, their low adsorption capacity, poor physical integrity, pre-treatment requirements and their low effectiveness make operation and maintenance very difficult and required frequent regeneration (Hai-Xia Wu 2011; Zhao et al., 2012).

Some of the challenges faced when using low cost natural materials is their unsuitability when used on large scale operations and variability in the quality of the materials. In some cases the materials have poor physical characteristics which necessitate pre-treatment technology there by increasing the costs. In some cases the logistical costs in their collection also hinder their large scale use. In response, efforts have been devoted to the development of novel materials with high removal efficiencies as such man-made adsorbents with low cost and high adsorption capacity (Hai-Xia Wu 2011; Keyser et al., 2006; Mostafa et al., 2011). However, in these pieces of research the adsorbents developed were in fine powder from which present other problems during process scale up. It is known that ultra-fine powder adsorbents can be used directly for water treatment, however, issues due to their low hydraulic conductivity means, high pressure drop may occur in packed bed as well as leaching (Hai-Xia Wu 2011; Mostafa et al., 2011; Zhao et al., 2012). If the adsorbent material is used in fine

powder form, problems are also encountered when separating the adsorbent from the treated effluent to recover the adsorbent (Hai-Xia Wu 2011).

Efforts have been made to improve the performance of some adsorbents by engineering their physical and structural properties; for instance, increasing the particle size of the adsorbent make it suitable for use in packed column systems and reduces the pressure drop across the column (Hai-Xia Wu 2011; Keyser et al., 2006; Mostafa et al., 2011; Zhao et al., 2012). An earlier study also revealed that narrow size distribution particle favours lower pressure drop across the column (Keyser et al., 2006). Size enlargement unit operations such as granulation process provide an excellent opportunity for transforming the fine powdery adsorbent materials into a form that is suitable for large scale operations. The granulation process also makes it possible to improve the functionality of the adsorbent particles by incorporating other active components on the surface or internal structure of the adsorbent. The physical properties of the adsorbent particles such as mechanical strength and attrition resistance can be significantly enhanced by careful selection of formulation and processing variables during production (Corey et al., 1977; Hai-Xia Wu 2011; Tardos et al., 1997; Zhao et al., 2012).

The use of iron oxide or iron hydroxide or compounds containing these materials as adsorbents is not uncommon as there are several studies in the literature (Albadarin et al., 2014c; Aredes et al., 2013; Cope et al., 2014; Glocheux et al., 2014; Hai-Xia Wu 2011; Zhao et al., 2012). In a recent study iron-aluminium-cerium hydroxide (Fe-Al-Ce) adsorbent for removal of fluoride was produced using extrusion techniques (Zhao et al., 2012). In a separate research iron-aluminium and cerium trioxide adsorbent loaded onto a poly vinyl alcohol (PVA) matrix cross linked in boric acid, was used for removal of fluoride from synthetic wastewater (Hai-Xia Wu 2011). This study showed that a trade-off between adsorption capacity and stability has to be made; higher composition of PVA in the matrix increased the strength and stability of the matrix at the expense of adsorption capacity of the fluoride (Hai-Xia Wu 2011).

In this study, a preliminary test was conducted prior the production of iron oxide adsorbent granules in order to investigate the suitable solvent used for the binder. The granulation process is not trivial as it is affected by formulation variables, equipment variables such as impeller shape design and process variables (Mangwandi et al., 2011a; Mangwandi et al., 2012; Mangwandi et al., 2015; Mirza et al., 2015; P.C Knight, 2000; Rahmanian et al., 2011; Tardos et al., 1997). The solvents that were considered were acetone, methanol and toluene. The solvent loaded with the polyvinyl acetate (PVAc) binder was added to the iron oxide powder

and mixed. As the solvent evaporates from the binder, powder particles stick together with inter-particle bridges and undergo further growth mechanisms by forces in the mixer to produce granules. The granulation time was kept constant because of its insignificant effect in this study as an organic solvent was used. The volatility properties of the organic solvent make it easily to be evaporated regardless the duration of process. A face centred design of experimental design was employed to investigate the effect of process parameters such as impeller speed, liquid binder concentration and liquid-solid ratio on physical characteristics of the adsorbent. The response functions selected for this study were granular the product yield, granule strength, stability coefficient in water and mean diameter of the iron oxide adsorbent granule.

2. EXPERIMENTAL METHODS

2.1 MATERIALS

General reagent grade iron (II, III) oxide black powder was supplied by Mistral Chemicals, UK. Polyvinyl acetate (PVAc) pellets were purchased from Sigma Aldrich, UK. Acetone, methanol and toluene supplied by Sigma Aldrich, UK were used as solvents for PVAc.

2.2 PREPARATION OF BINDER

Different masses of PVAc pellets were added to 1000 g of solvent to obtain binder solutions with the desired concentrations of 6.5, 10, 15, 20 or 23.41 % (w/w) basis. The mixture of the pellets and solvent were continuously stirred in a sealed container until all the PVAc pellets were dissolved. In the preliminary experiments the PVAc concentration in binder solutions was kept at 20 % (w/w). For the remainder of the batches, the concentration was 6.5, 10, 15, 20 or 23.41 % (w/w) depending on the batch being prepared.

2.3 PRODUCTION OF GRANULES

The granules were produced in a high shear granulator, Kenwood KM070, which equipped with two blade impeller and stainless steel mixing bowl. A central composite design (CDD) of experiment was used to investigate the effect of process and formulation variables (impeller speed, binder concentration and liquid to solid ratio) on the adsorbent granules. The design has 6 centre points and 14 non-centre points resulting in a total of 20 runs and the design was rotatable with a default alpha value of 1.681. The values of the three input variables at the different levels of setting are shown in Table 1. The granulation time was kept constant at 3 minutes, and only acetone was used as the solvent for poly vinyl acetate to prepare the binder solutions. The mass iron oxide powder was kept at 300g.

2.4 GRANULES CHARACTERIZATION

2.4.1 GRANULE SHAPE ANALYSIS FROM MICROSCOPIC IMAGES

Representative random samples of granules were selected from the different batches and digital images of these granules were taken using a digital microscope (Keyence Digital Microscope, VHX-5000, Keyence UK). Images were taken at different magnifications to reveal the surface structure of the granules.

2.4.2 PARTICLE SIZE ANALYSIS AND DETERMINATION OF PRODUCT YIELD

The granules characterization analysis was conducted in terms of granules size distribution, granule strength, stability coefficient and mean diameter, d_{50} . A total of 12 sieves with aperture sizes ranging from 0.106 to 4 mm were used in the determination of the granules size distributions of the samples. The sieving trays were placed on the Stuart Mini Orbital Shaker for 5 minutes at 180 rpm to determine the granules and mass mean diameter of the granules. The mean diameter of the granules and the product yield were determined from the sieve analysis data using Eqs. (1) and (2) respectively;

$$d_{mean} = \frac{\sum_{i=1}^{12} x_i m_i}{\sum_{i=1}^{12} m_i} \quad Eq (1)$$

In Eq (1) x_i and m_i are arithmetic average size of interval i and mass of granules in interval i , respectively.

$$\eta = \left(\frac{m_p}{M_T} \right) \times 100 \quad Eq (2)$$

The symbols m_p and M_T in Eq (2) represent mass of granules in the size range of the product and total mass of granules in the batch, respectively.

Based on the dimensions of the adsorption column to be used in the detailed adsorption study, the size of the granules used ranged from 1.4 to 1.7 mm.

2.4.3 DETERMINATION OF GRANULE STRENGTH

The strength of granules was determined using a Texture Analyser (TAXT2i, Micro Stable Systems, UK). The strain rate effect on the granule strength was investigated prior to the strength analysis tests. Compression test were carried out at compression speeds of 0.5, 2.5, 5

and 7.5 mm/min. The results show that effect of strain rate in this range was insignificant (see Figure 1). Subsequent compression tests were all done at a compression speed of 5mm/min. The granules strength was determined from diametric compression of the single granules using method described previously (Mangwandi et al., 2010; Mangwandi et al., 2013a). The granule strength was determined from the failure load and granule diameter, in this case the diameter was taken as the distance between the two platens when the first contact is made between the moving platen and the granule (Hiramatsu & Oka, 1966; Mangwandi et al., 2013a).

$$\sigma = 2.8 \times \left(\frac{F_{\max}}{\pi d^2} \right) \quad \text{Eq (3)}$$

where σ is granules granule strength, F_{\max} the failure load and d is granule diameter.

2.4.4 WATER STABILITY TESTS

Samples of granules in the targeted size range of a known mass, m_0 , were added to glass jars containing distilled water (50 mL). The samples were left on a mechanical shaker (Gerhardt typeLS5) over a period of 72 hours at 100 rpm. At the end of the test period, the granules were filtered from the solutions and dried. The mass of the granules remaining at the end of the tests was measured (m_t).

The stability coefficient, λ , was determined from;

$$\lambda = \frac{m_t}{m_0} \quad \text{Eq (4)}$$

High values of stability coefficient, λ , indicate that the granules are highly stable in water.

Similar tests were also performed under different conditions of pH values of 2, 6 and 10, which are typical pH of wastewater; in order to investigate the leachability of the PVAc binder. The mass loss of the granules during the test was used as indicator of leachability of the granules. For all the samples tested that amount of PVAc leached into the water was negligible.

2.4.5 DETERMINATION OF IRON OXIDE COMPOSITION

The composition of the iron oxide in the granules was determined gravimetrically by measuring the mass of residue formed upon removal of the binder particles from the granules. The binder PVAc is soluble in acetone; the known mass of granules (~500 mg) was added to 10 ml of acetone. This was sonicated in sonic bath (Elmasonic S30, Elma Schmidbauer GmbH, Germany) for 5 minutes, after sonication the samples were filtered and dried. The complete

removal of the binder was confirmed by the FT-IR analysis as discussed in section 2.1. The percentage iron oxide in the samples was calculated from the initial sample mass and mass of residuals after sonication and drying. All the tests were done in triplicates.

2.4.6 CONTACT ANGLE MEASUREMENTS

The interaction between the iron oxide granules with water was investigated by measuring contact angle on the surface of a disk prepared from the granules. 500 mg of iron oxide granules were compressed in to flat discs using a manual hydraulic press (Atlas 15 T Hydraulic Press, Specac Inc., USA) using procedure described previously (Mangwandi, 2015). The contact angles on the prepared disks surfaces with water droplets were measured using a FTA1000B goniometer instrument (First Ten Angstroms, Ltd). The FTA 1000B goniometer was composed of a camera, a stage-sample holder, a drop dispenser with a syringe and needle and a backlight. It used proprietary FTA32 software to control the height of the drop dispenser and the volume of the water drop and thus determine the contact angle (Sang et al., 2015).

2.4.7 FT-IR ANALYSIS OF THE GRANULES

The FT-IR analysis was performed using a Perkin–Elmer Spectrum 100 spectrophotometer to identify the functional groups available on the granules surface from the different samples and iron oxide powder (KBr technique). Spectra within the range of 400–4000 cm^{-1} were recorded.

For pure iron oxide, Figure 2 indicates the presence of absorption bands: around 3400 cm^{-1} due to O–H stretching, vibrations and stretching of Fe–O bonds (602 cm^{-1} and 1650 cm^{-1}) which is in agreement with the literature values (Basavaraja S. et al., 2011). After PVAc addition, it can be clearly seen the new absorption bands of C=O and C–O groups at 1727 cm^{-1} and 1220 cm^{-1} , respectively. These absorption bands are absence in the residual after the removal of PVAc. The composition of the iron oxide in the granules was obtained by calculating the weight-difference of the samples before and after removal of PVAc from the granules. PVAc was removed from the granules by dissolving the granules in acetone and drying them completely in oven to constant weight. The residual particles were then weighed to ensure complete removal of PVAc was confirmed by comparing FT-IR spectra of the residuals with that of pure iron oxide typical comparison of the spectra is shown in Figure 2.

2.5 DETERMINATION OF ARSENIC REMOVAL

The adsorbent granules were contacted with synthetic water solutions containing arsenic (III) and arsenic (V) for 3 days. The initial concentrations of the solutions were 1000 ppb. At

the end of the test, arsenic concentrations were determined using ICP-ES. The removal efficiency of the adsorbent was determined using Eq. (5).

$$R = \left(\frac{C_0 - C_e}{C_0} \right) \times 100\% \quad \text{Eq (5)}$$

where C_0 and C_e are the initial and equilibrium concentration of the arsenic ions.

3 RESULTS AND DISCUSSION

3.1 PRELIMINARY TEST ANALYSIS – SELECTION OF SOLVENT FOR THE BINDER

The experiments with binder solutions obtained from different solvents showed that acetone was the best solvent of the three. The granule size distributions of the batches are presented in Figure 3.

The highest product yield (~70 %) was obtained when acetone was used as the binder followed by toluene (~40 %) and then methanol (~25 %). Furthermore, the strength of granules prepared using the acetone binder solution was also superior. Hence, polyvinyl acetate-acetone solution was selected as a binder solution.

3.2 GRANULE SHAPE AND SURFACE STRUCTURE ANALYSIS

Figure 4 shows images of iron oxide granules from the batches 5, 10, 15 and 20. It is evident from this figure that there are no huge differences in the shapes of the granules. All granules from the samples analysed showed some bright spots which could be some solidified polyvinyl acetate particles from the binder. As can be seen from the images presented in Figure 5 the surfaces of the granules were rough with some pores visible on the surface. The surface roughness of the granules seems to suggest that the main granule growth mechanism in this particular case was coalescence.

3.3 EFFECT OF PROCESS VARIABLES ON PRODUCT YIELD

In this work, the product yield has been defined as the mass fraction of granules in the target size range 1 to 2 mm. The summarized results of granules product yield from 20 batches of granulation for iron oxide granular production is shown in Figure 6 which represents the highest product yield approximately 40% was obtained for Run 4.

In Run 4, the maximum amount binder concentration (23.4 g/L) was used whilst the impeller speed and liquid to solid ratio was in the medium range (131.5 rpm and 0.25 respectively). The lowest product yield approximately 15.5% was obtained for Run 14 when a low binder

concentration was used (10 g/L) whilst the maximum impeller speed (160 rpm) and high liquid to solid ratio, 0.30.

The effect of the process variables on the granules product yield is summarized by the empirical model as shown below in Eq (6).

$$(\eta)^{-1.13} = [0.0855 + 1.287 \times 10^{-3} C_{pva} + 3.817 \times 10^{-5} \Omega - 1.289 \times 10^{-1} \gamma] \quad Eq (6)$$

where C_{pva} is concentration of PVAc in the binder, Ω is the rotational speed, γ is the liquid to solid ratio.

Figure 7 show a surface plot obtained by using Eq (6) for two different values of liquid to solid ratios (i.e. $\gamma = 0.15$ and $\gamma = 0.33$). For the case when the liquid to solid ratio is high ($\gamma = 0.33$), the product yield varies from around 30 % to about 55%. The maximum yield is obtained when the granulation is done at high impeller speed using a granulating liquid with high concentration of PVAc binder. It can also be noted that relative increases in the product yield with respect to change in impeller speed increases with increasing binder concentration.

During granulation, there are competing mechanisms occurring at any given time and these include granules growth, consolidation and breakage (Iveson et al., 2001; Mangwandi et al., 2013a). According to a previous study (Mangwandi et al., 2013a), the rate at which these processes occur depends on a number of process variables. In this work, the binder concentration, impeller speed and liquid to solid ratio are the process variables with a constant granulation time. The balance between the competing constructive and destructive forces will determine the overall population of particles in any given size range (Mangwandi et al., 2013a).

The more concentrated binder solution corresponds to a more viscous one. It has been discussed that increasing the binder viscosity increases the viscous forces between particles, hence, generally influence the rate of consolidation (Iveson et al., 2001; Rahmanian et al., 2011). However, too high binder viscosity may retard the migration of liquid binder to the surface. It then reduces the pore saturation, hence, inhibits the granule growth (Iveson et al., 2001). On the other hand, the binder viscosity affects both the rate of size enlargement and the mechanism of size enlargement (Mills et al., 2000). Granulation at low viscosities is believed to be controlled by layering growth mechanisms while at higher viscosities result in a coalescence growth mechanism (Chitu et al., 2011; Mangwandi et al., 2010). This might explain why the highest granules product yield was obtained when high binder concentration was used.

It is evident from Figure 7 that increasing the liquid to solid ratio, which increases the amount of binder available for forming liquid bridges between powder primary particles, increases the product yield (Mangwandi et al., 2013a; Mangwandi et al., 2013b). Also, it can be seen that at the highest liquid to solid ratio (0.33), the granules product yield has significantly increased with increasing the impeller speed when high liquid binder concentration is used. However, a slight increase in the product yield with increasing impeller speed is observed at low binder concentration. Almost the same pattern of surface response plot can be seen but the granules product yield decreased by about 50% when liquid to solid ratio is lowered to 0.15. However, the rate of increase in the product yield with respect to changes of binder concentration or impeller speed is significantly reduced.

The granules coalescence growth can be due to either by coalescence of non-deformable granules or coalescence of deformable granule. For non-deformable granules coalescence will only occur if there is a liquid layer present at the surface to bind them (Iveson et al., 2001). For deformable granules coalescence occurs of even without liquid layer on the granule surfaces, the collision energy is dissipated through plastic deformation that creates an area of contact which holds the granules together (Iveson et al., 2001).

Increasing the impeller speed may promote granule growth, though, it may also result in increased breakage of the granules (Iveson et al., 2001). High impeller speed, regardless of the binder viscosity, may influence the granules' deformability either breaking into fines or further growth into coarse granules (Mangwandi et al., 2013a). From Figure 5, it is clear that increasing in impeller speed results in increasing granules product yield and the effect of changing the impeller speed is more pronounced when the liquid to solid ratio is high ($\gamma = 0.33$) and high binder concentrations (20 g/L). At low binder concentrations, the effect of the impeller speed is less prominent; this is due to the rate of breakage being significant due to formation of weaker bonds when less viscous binder is used. It can be assumed that the extent of granules breakage was significant and that it limits the overall growth (P.C Knight, 2000).

Using low viscous binder solutions during the granulation process results in formation of weak bonds between the primary particles. Figure 6 has shown that the effect of impeller speed on the granules product yield is also dependent on the binder viscosity. The increase in impeller speed results in an increase in granules product yield and the effect is more pronounced when more binder is used in the process (higher liquid to solid ratio).

3.4 EFFECT OF PROCESS VARIABLES ON GRANULES GRANULE STRENGTH

The results from strength analysis of granules in the targeted size range are shown in Figure 8. The figure shows that granules with the highest strength were produced in batch number 20 where the average strength of the granules was found to be around 25 MPa. For batch 20, impeller speed was set at 160 rpm; binder concentration was 20 g/L; and the liquid to solid ratio of 0.30 were used. The weakest granules (~5 MPa) were produced in batch number 3 where the liquid to solid ratio was at the minimum value of 0.17.

ANOVA analysis of the granule strength data showed that the binder concentration and liquid to solid ratio strongly affect the strength of the granules. In the range of impeller speeds used here, the impeller speed had little effect on the strength of the granules. The effect of the process variables on the granules product yield is summarized by the following empirical model;

$$\sigma = -15.45 + 0.9987 C_{pva} + 3.425 \times 10^{-3} \Omega + 53.775 \gamma \quad Eq (7)$$

Figure 9 shows surface plots for liquid to solid ratios of 0.22 and 0.30. It can be seen that an increase in the binder concentration results in increasing granules strength. It has been demonstrated that high binder viscosity increases the potential to form granules of high strength due to hydrodynamic forces of liquid bridges between particles is proportional to the viscosity (Mangwandi et al., 2010; Rahmanian et al., 2011). It simply indicates that more viscous binders formed liquid bridges with have stronger internal dynamic forces between the particles (Mangwandi et al., 2010; Mangwandi et al., 2012; Rahmanian et al., 2011).

3.5 EFFECT OF PROCESS VARIABLES ON GRANULES STABILITY COEFFICIENT

The granules stability coefficient was used to evaluate the stability of granulated iron oxide in distilled water. The summarized results of granules stability coefficient from 20 batches of iron oxide granular production is shown in Figure 10. The results presented in Figure 10 show that the stability coefficient ranges from 0.75 to about 0.99. According to these results, the most stable granules were those produced in batch number 7 and the least stable were those from batch number 18.

The effect of the process variables on the granules stability coefficient is summarized by the empirical equation.

$$\lambda = -0.752 + 3.321 \times 10^{-2} C_{pva} + 5.345 \times 10^{-3} \Omega + 1.098 \times 10^1 \gamma + 2.497 \times 10^{-4} C_{pva} \Omega - 8.096 \times 10^{-2} C_{pva} \gamma - 2.64 \times 10^{-3} C_{pva}^2 - 4.429 \times 10^{-6} \Omega^2 - 14.763 \gamma^2 \quad Eq (8)$$

The influence of the process variables on the granules stability coefficient is summarized by the surface plots in Figure 11 for the case where the liquid to solid ratio is 0.30. It is expected that granulation at higher impeller speed would result in the formation of strong dense granules that would have high stability. Interestingly, this is not what was always observed; at lower binder concentration, increasing the impeller speed actually results in a slight reduction in the stability coefficient of the granule. At a higher binder concentration, a slight increase in the stability of the granules was observed. It has been explained that the use of low viscosity binders in a high shear mixer at high impeller speed increases the amount of breakage and shear which delayed densification, resulting in less-spherical granules with a higher porosity (Mangwandi et al., 2010).

3.6 EFFECT OF PROCESS VARIABLES ON GRANULES MEAN DIAMETER

Analysis of the average granules sizes from the 20 batches using ANOVA revealed that the binder concentration and amount of binder used during the granulation are the most significant factors affecting the average size of the granules. The empirical equation obtained from the analysis is as follows.

$$(d_{mean})^{-0.45} = [1.142 + 5.73 \times 10^{-3} C_{pva} + 1.49 \times 10^{-3} \Omega - 1.97 \gamma] \quad Eq (9)$$

The surface plots generated from Eq. (9) are shown in Figure 12. This figure shows the effect of impeller speed, binder concentration and liquid to solid ratio on the size of the iron oxide adsorbent granules formed during granulation. Two surfaces are shown for the different values of liquid to solid ratio, as expected at higher liquid to solid ratios larger granules are produced. When the liquid to solid ratio is 0.22 the average size of granules ranges from 0.9 mm to about 1.1 mm whereas at higher level (0.30) the average size ranges from 1.2 to around 1.6 mm. This can be attributed to an increase in the amount of binder available for granule formation at higher liquid to solid ratio (Iveson et al., 2001). It can be observed from Figure 8 that as the impeller speed is increased the average size of the granules decreases suggesting that at the levels of binder viscosity used here, granule breakage of outweigh growth.

3.7 SURFACE AREA OF THE GRANULES

The surface area of the granules was obtained from N₂ adsorption measurements performed at liquid nitrogen temperature, 77 K and by means of the Brunauer, Emmett and Teller (BET) equation. The surface areas and pore radius of the granules from the four samples E5, E10, E15 and E20 are presented in Table 2. It can be seen from the table the surface areas of the granules are of the same order of magnitude ranging from 10 to 12 m²/g.

3.8 IRON OXIDE COMPOSITION OF SELECTED SAMPLES

The composition of the iron oxide – PVAc granules in the targeted size range was found to range between 88 and 93%. The variation in the iron composition is linked to the different concentrations of the binder solutions and the difference in the amount of binder added during the granulation process i.e. different liquid to solid ratio.

3.9 IRON OXIDE COMPOSITION OF SELECTED SAMPLES

Typical images captured during the measurement are shown in Figure 13. The values of the contact angles for the four samples were approximately 90° suggesting that the granules surfaces were almost hydrophobic in nature. Statistically no significant difference was observed in the wettability of the granules from the different samples.

3.10 IRON OXIDE GRANULES AS ARSENIC ADSORBENT

Granules in the targeted size range were selected from four batches (No. 4, No 10, No. 15 and no. 20) were used in preliminary adsorption tests for removal of As(III) and As(V) at 1000 ppb. In the adsorption test the pH of solutions were unaltered and were not controlled. The results from the test are shown in Figure 14 and it can be seen that removal of As (V) was ranging from 3 to 70 %. Granules from batch number 10 had the least removal of As (III) whilst the percentage removal from the other three batches ranged from 65 to 70 %. Granules from batch 10, with a percentage removal of about 70 % out-performed the other batches when it came to removal of As (V) ions. The removal capacity of the As(III) is positively correlated to the concentration of iron oxide in the granules as can be seen in Figure 15.

In a recent study, maximum removal efficiencies ranging between 70 and 80 percent were achieved for the removal of As(III) using lipodocrocite crystals at initial concentration 100 ppb and pH of about 9 (Wang & Giammar, 2015). The removal efficiency obtained in the present study are lower than those several reports in literature where high arsenic removal efficiencies of up to 99 % have been reported (Aredes et al., 2013; Cope et al., 2014; Glocheux et al., 2014; Lunge et al., 2014; Maji et al., 2011; Salameh et al., 2015; Yürüm et al., 2014). The difference

in the removal efficiencies could be due to the fact that dosage levels of the adsorbent that was used in the other studies were about 10 times higher than used in the current studies. The granular iron oxide granules show good potential considering that the iron oxide was granulated as received without any modification or enhancement. Also the adsorption tests were carried out without any pH adjustment as the objective was to select the best samples from batches produced.

4 CONCLUSION

A granular iron oxide adsorbent was successfully prepared and the effects of process and formulation variables on the physical characteristics of the granules were investigated. The concentration of the PVAc in the granulating liquid and the mass of binder added per unit mass of the dry powder (liquid to solid ratio) were found to be the main variables controlling the size, mechanical strength and stability of the adsorbent granules. The results from preliminary adsorption studies indicate that about 70 % removal of As(III) and As(V) can be achieved without any pH adjustment when the initial concentration of the arsenic was 1000 ppb. More detailed adsorption studies will be considered in future work.

LIST OF SYMBOLS

C_0	<i>Initial concentration of arsenic</i>	[ppb]
C_e	<i>Concentration of arsenic in solution at equilibrium</i>	[ppb]
C_{pva}	<i>Concentration of PVAc binder in solution</i>	[g/L]
d	<i>Granule diameter</i>	[m]
d_{mean}	<i>Mean size of the batch</i>	[m]
F_{max}	<i>Maximum force required to break the granule</i>	[N]
m_i	<i>Mass of granules in interval i</i>	[kg]
m_t	<i>Mass of sample after a time t</i>	[kg]
m_0	<i>Initial mass of sample</i>	[kg]
m_P	<i>Product mass</i>	[kg]
m_B	<i>Total mass of granules produced per batch</i>	[kg]
R	<i>Removal efficiency</i>	[%]
x_i	<i>Average particle size of interval i</i>	[mm]

Greek symbols

γ	<i>Liquid to solid ratio</i>	[-]
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η	<i>Product yield</i>	[%]
λ	<i>Stability coefficient</i>	[-]
Ω	<i>Impeller speed</i>	[rpm]
σ	<i>Granule strength</i>	[Nm ⁻²]

1

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12 hydroxide as a fluoride adsorbent using the extrusion method. *Chemical Engineering*
13 *Journal* **185–186** 211–218.

1 Table 1. Summary of experimental variable values used in the CCD design.

Variable	Setting				
	Low (-1)	Med (0)	High (+1)	$-\alpha$	$+\alpha$
Concentration (g/L)	10	15	20	6.6	23.4
Impeller speed (rpm)	103	131.5	160	83.6	179.4
Liquid/solid (-)	0.2	0.25	0.3	0.17	0.33

2

3

1 Table 2: List of experiments used in the Design of Experiment.

Run	Factor 1	Factor 2	Factor 3
-	A: Conc. [g/L]	B: Speed[rpm]	C: l/s ratio [-]
1	15.00	131.50	0.25
2	6.59	131.50	0.25
3	15.00	131.50	0.17
4	23.41	131.50	0.25
5	10.00	103.00	0.30
6	15.00	131.50	0.25
7	15.00	83.57	0.25
8	15.00	131.50	0.25
9	20.00	103.00	0.20
10	15.00	179.43	0.25
11	20.00	103.00	0.30
12	15.00	131.50	0.33
13	15.00	131.50	0.25
14	10.00	160.00	0.30
15	15.00	131.50	0.25
16	10.00	103.00	0.20
17	15.00	131.50	0.25
18	10.00	160.00	0.20
19	20.00	160.00	0.20
20	20.00	160.00	0.30

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2 Table 3: Summary of granule porosity, mean pore diameter and iron oxide composition of the granules.

Sample ID	Surface area (m ² /g)	Mean pore diameter (nm)	% Iron Oxide (w/w)
E4	12.17	28.19	88.3
E10	11.38	29.26	94.6
E15	10.54	29.53	91.3
E20	12.86	28.44	92.8

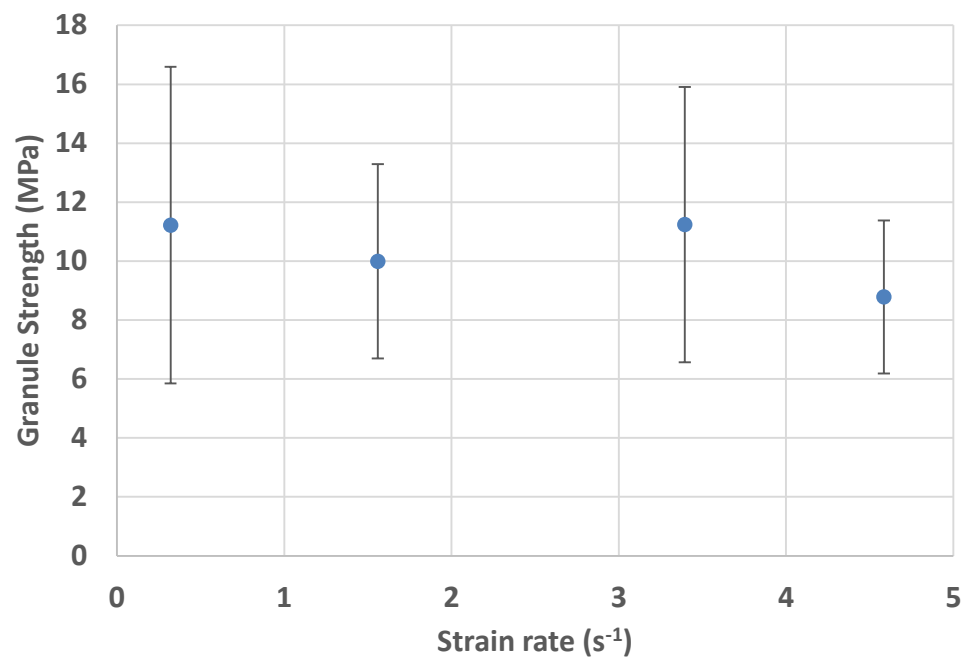
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1 Table 4. Comparison of the removal efficiency of the granules produced in the current work with similar materials
 2 from literature.

Material	Conc. range	Dosage	Removal Efficiency (%)	Reference
Magnetic Iron oxide (Fe ₃ O ₄) with tea waste	2 ppm	1 g/L	98-99	Lunge et al. 2014
Iron Oxide minerals	20 ppm	50 g/L	75 - 100	Aredes at al. 2013
Granular Iron oxide	1000 pbp	1 g/L	30 – 70	Current study
Porous Iron oxide	0.75 ppm	20g /L	30-90	Yürüm et al. 2014
Lepidocrocite	10 ppm		50 – 80	Wang et al. 2015

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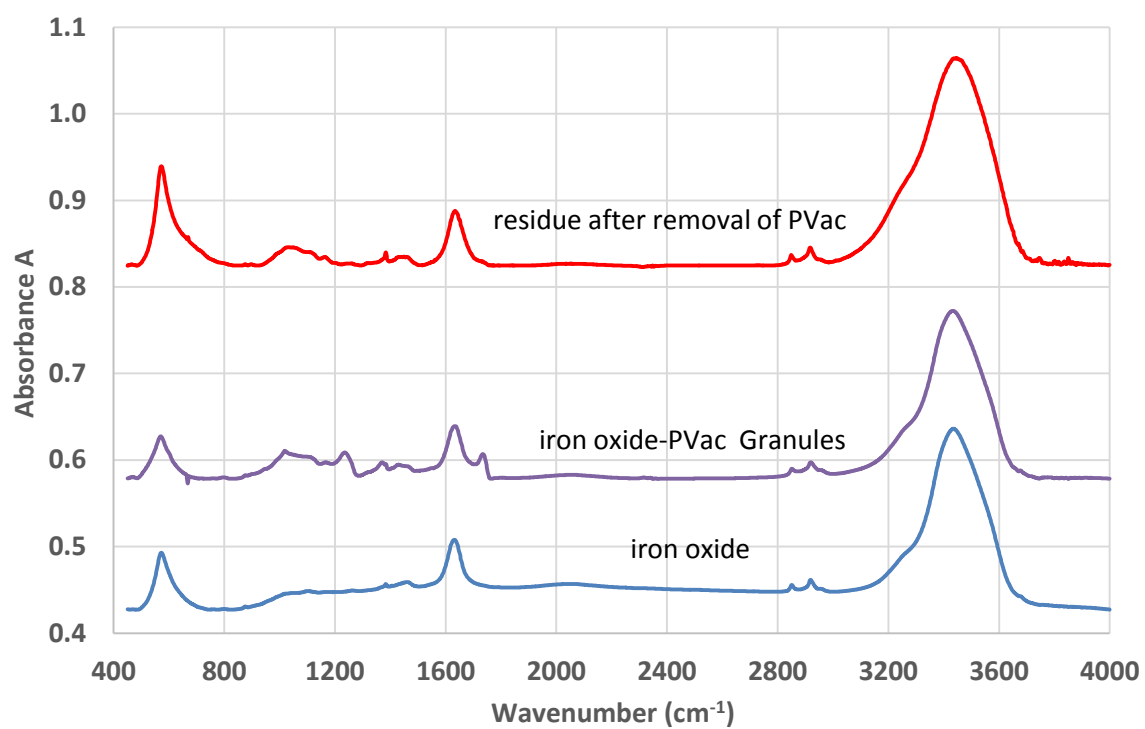


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2 Figure 1. Effect of strain rate (compression speed) on the granule strength.

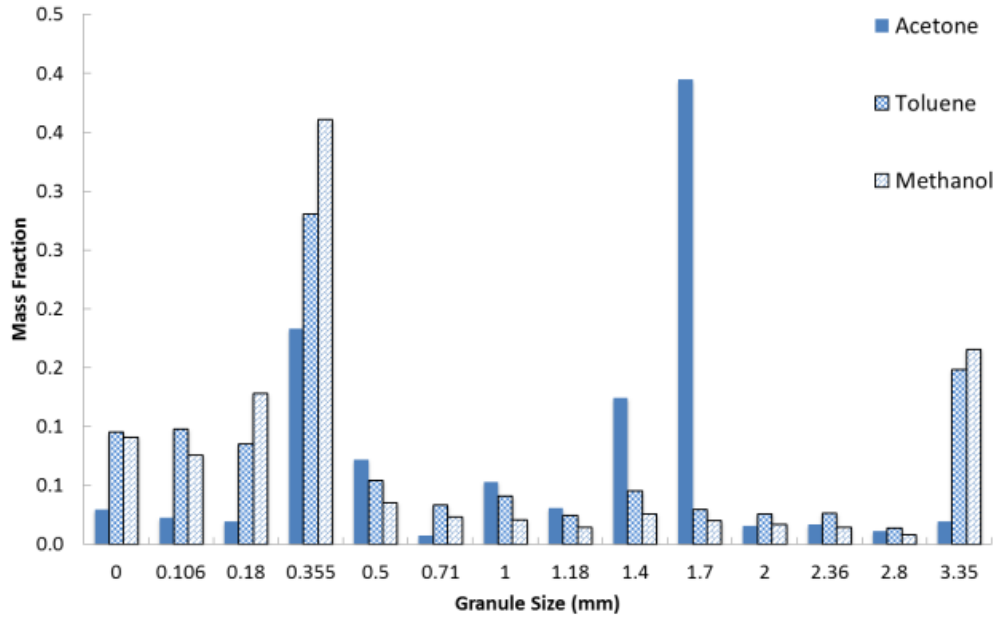
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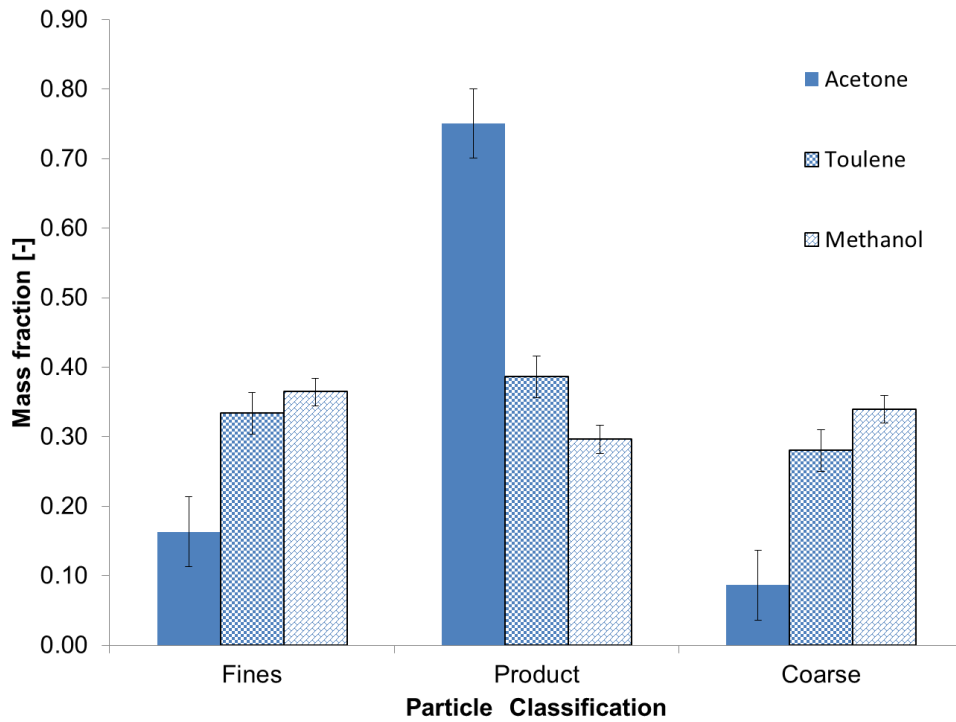


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3 Figure 2: comparison of FTIR spectra of raw iron oxide powder, iron oxide PVAc granules and residual after
4 removal of PVAc



(a)



(b)

Figure 3: Comparison of the granule size distributions of batches produced with PVAc binder dissolved in different solvents (a) comparison of product yield from the different batches (b). N.B. Fines refer to granules smaller than 1 mm, Product refers to granules in the size range 1 to 2 mm and Course refers to granule larger than 2mm.

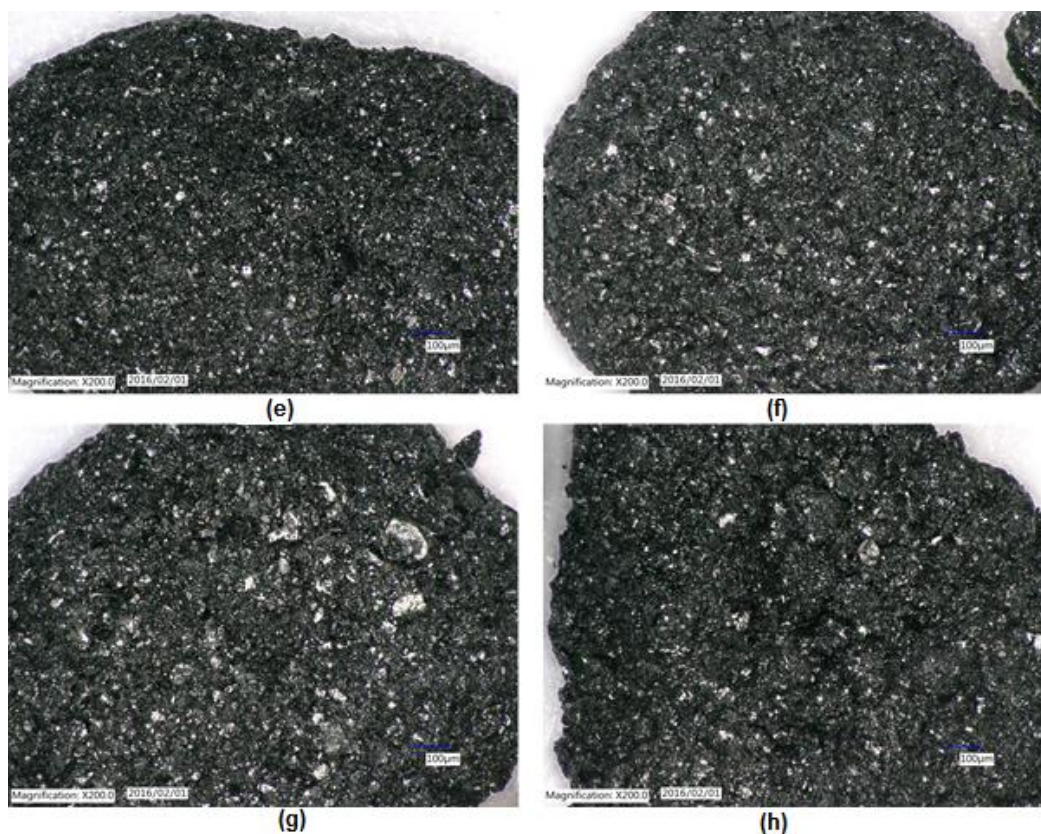
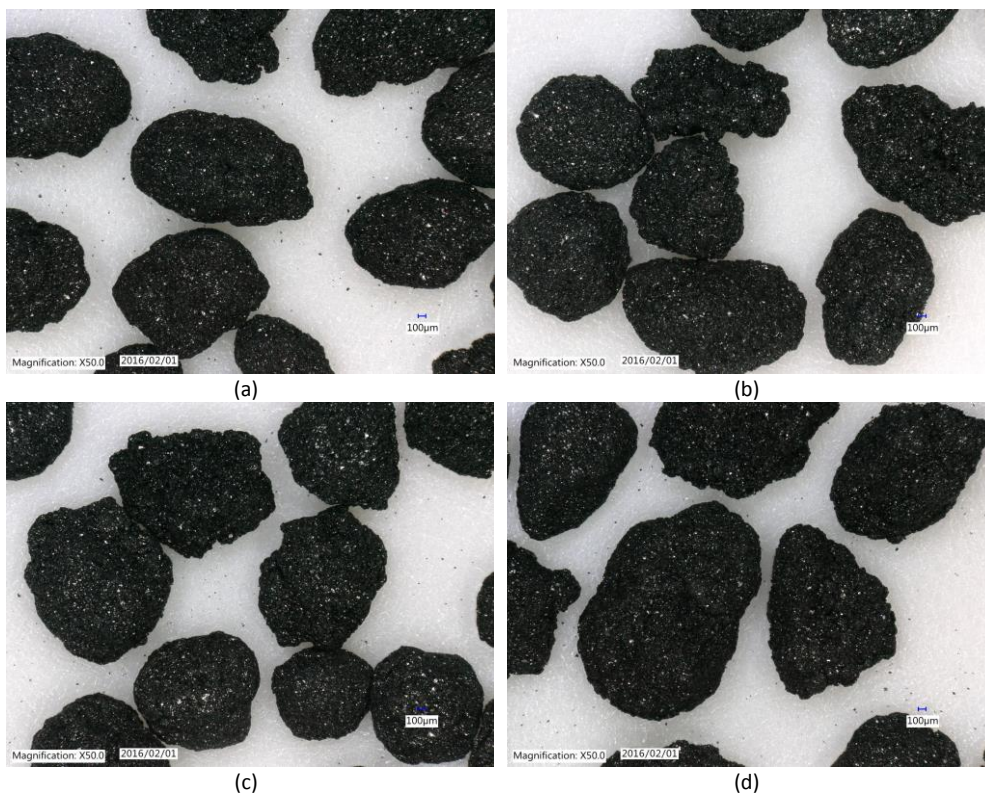
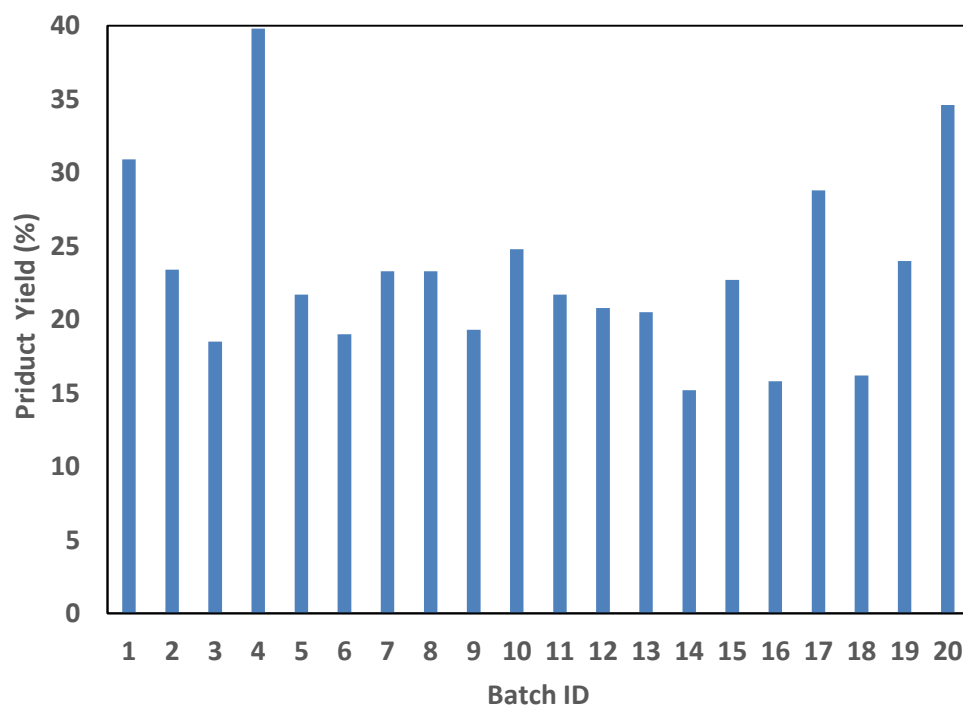


Figure 4: Images showing typical granules from different batches (a) Batch 5 (b) Batch 10 (c) Batch 15 and (d) Batch 20. Digital images showing taken at magnification of X200 of single random granules taken from different batches (e) Batch 5 (f) Batch 10 (g) Batch 15 and (h) Batch 20. Images taken using Digital Microscope – Keyence VHX 5000.

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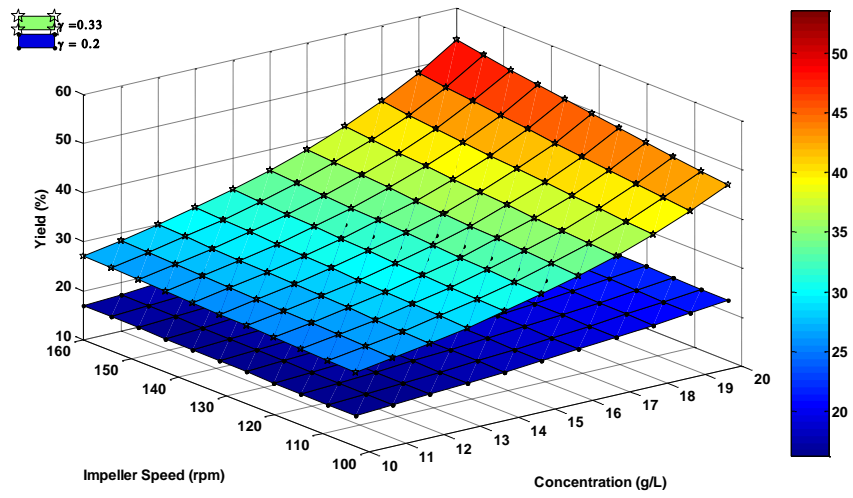


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4 Figure 5: Summary of the product yields from the 20 batches of granule produced.

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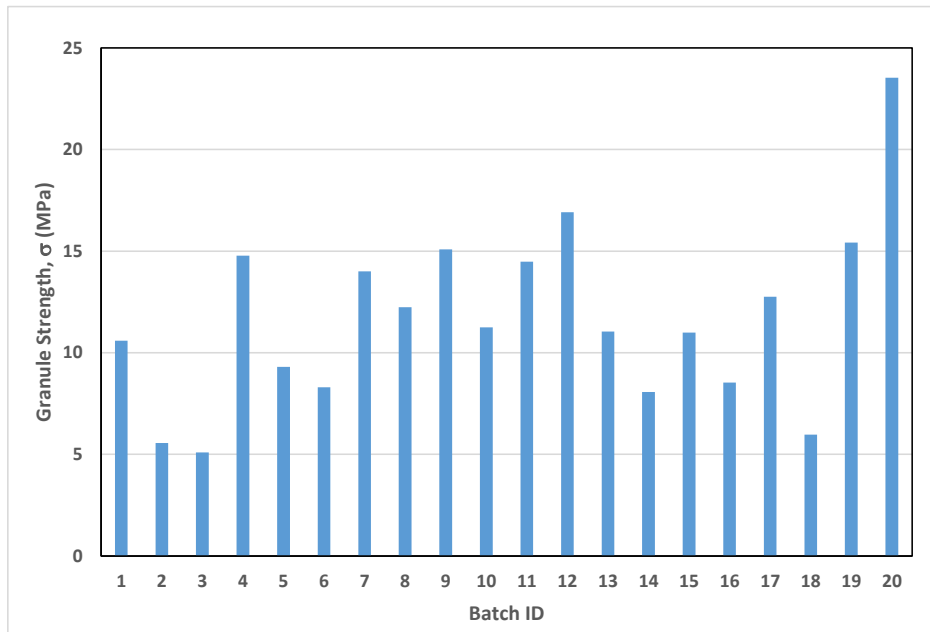
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3 Figure 6. Surface plots showing the effect of impeller speed and binder concentration at two different values of
4 liquid to solid ratios; $\gamma = 0.2$ and $\gamma = 0.33$.

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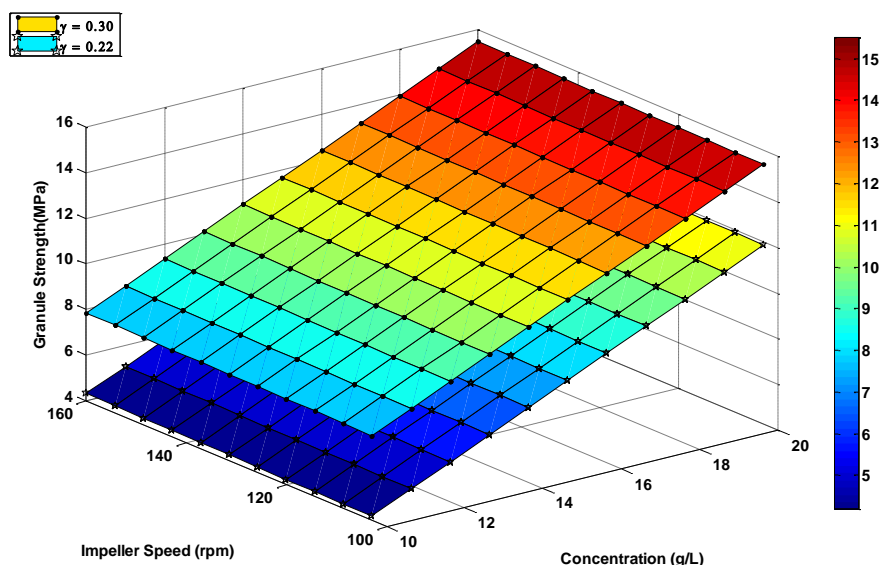


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4 Figure 7. Summary of granule strength of the granules from the different batch. Each data point is an average of
5 25 repetitions.

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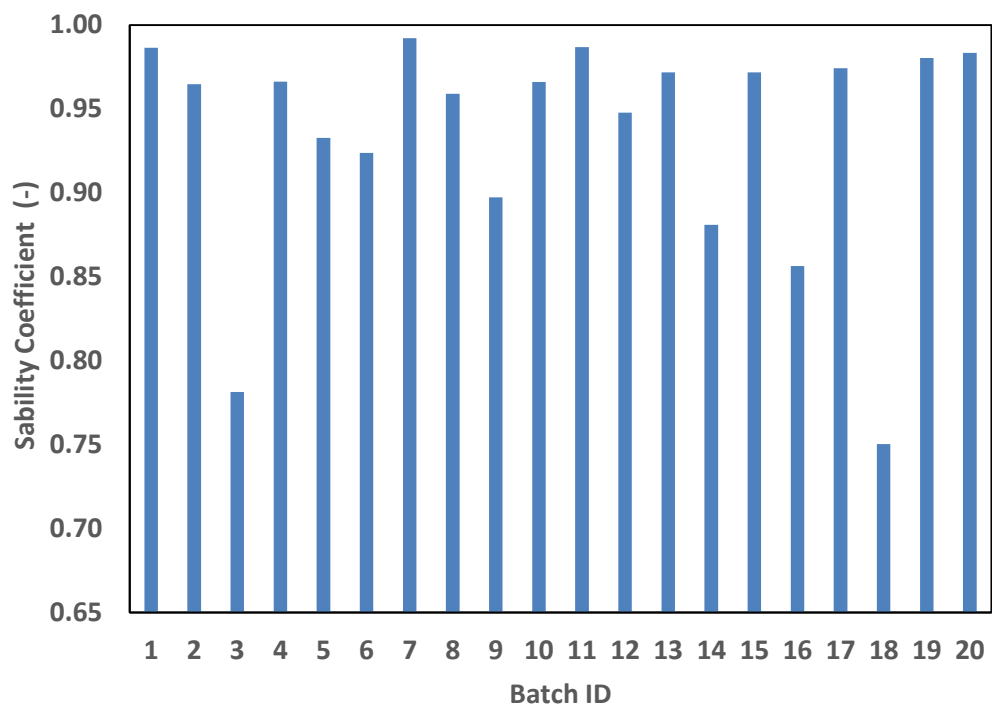
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3 Figure 8. Surface *plot showing the effect of the process variable on average force required to break the granules*

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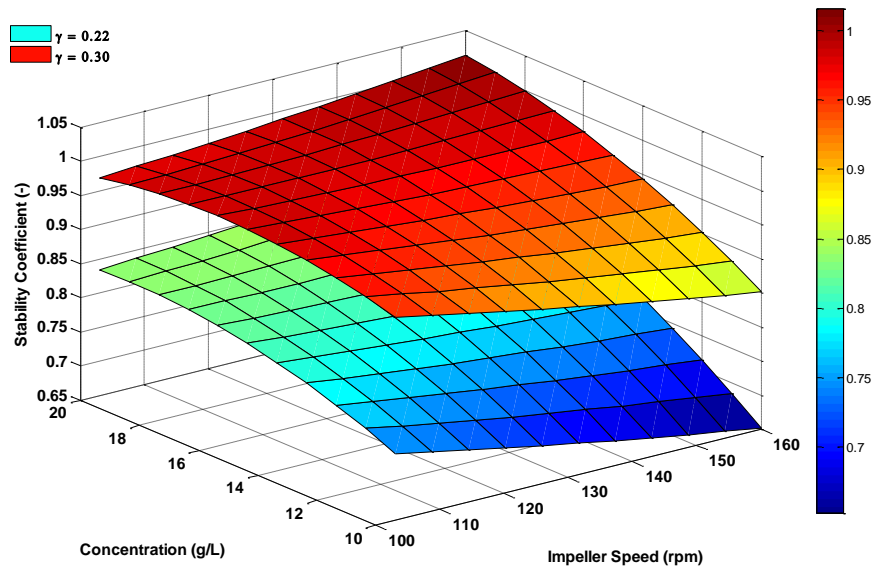


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4 Figure 9. Variation of granule stability coefficient across the 20 batches. Samples 7 and 18 exhibit the highest and the least
5 stability coefficients respectively.

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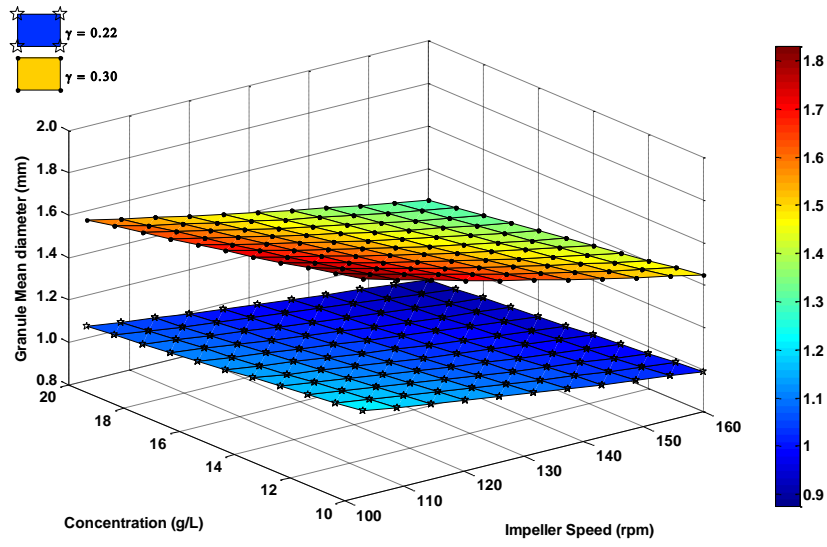


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3 Figure 10. 3D surface plot showing effect of process variables on granules stability coefficient at liquid to solid ratio of 0.33.

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3 Figure 11. Effect of process variable on the mean size of the granules.

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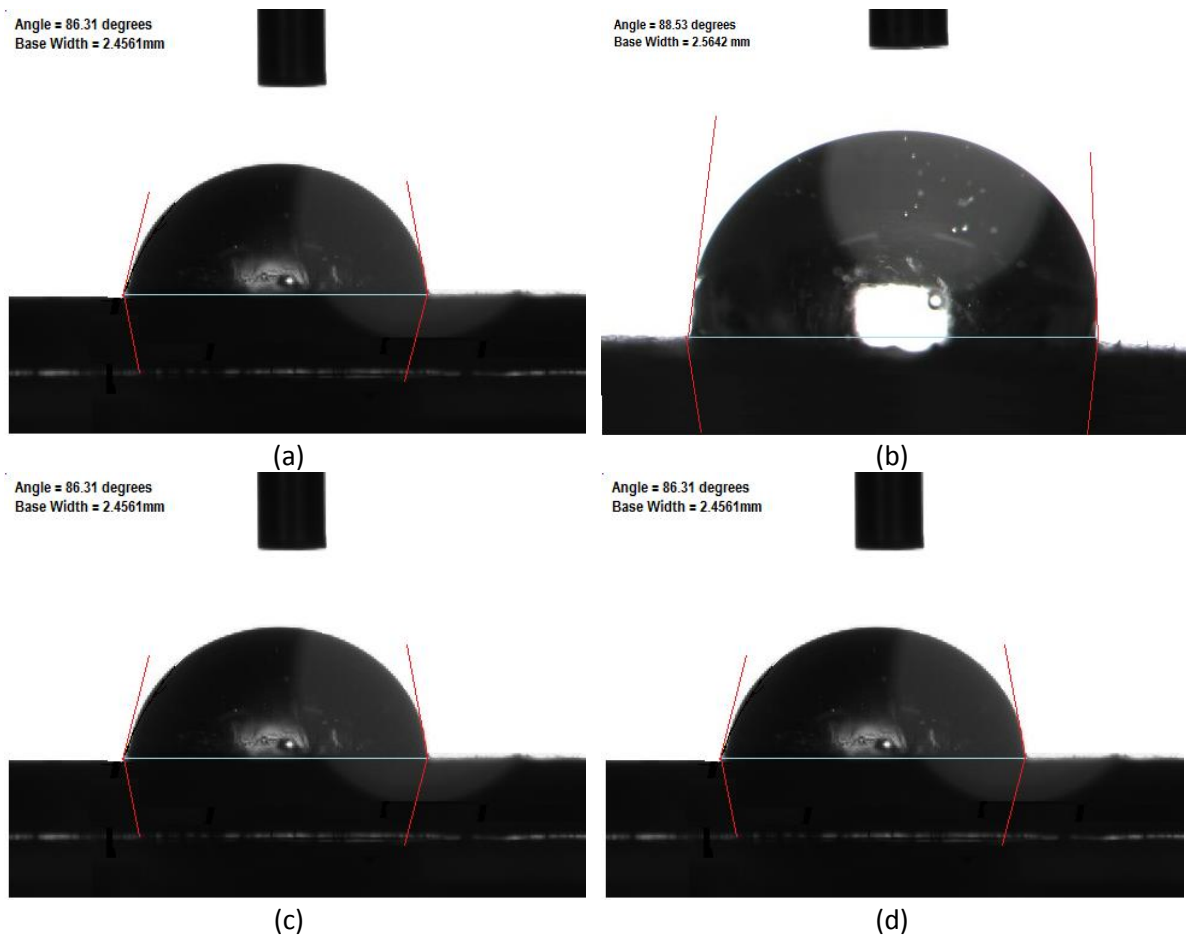


Figure 12: Typical images from contact angle measurements of water of surfaces disks from different samples of adsorbent granules (a) E4 (b) E10 (c) E15 and (d) E20.

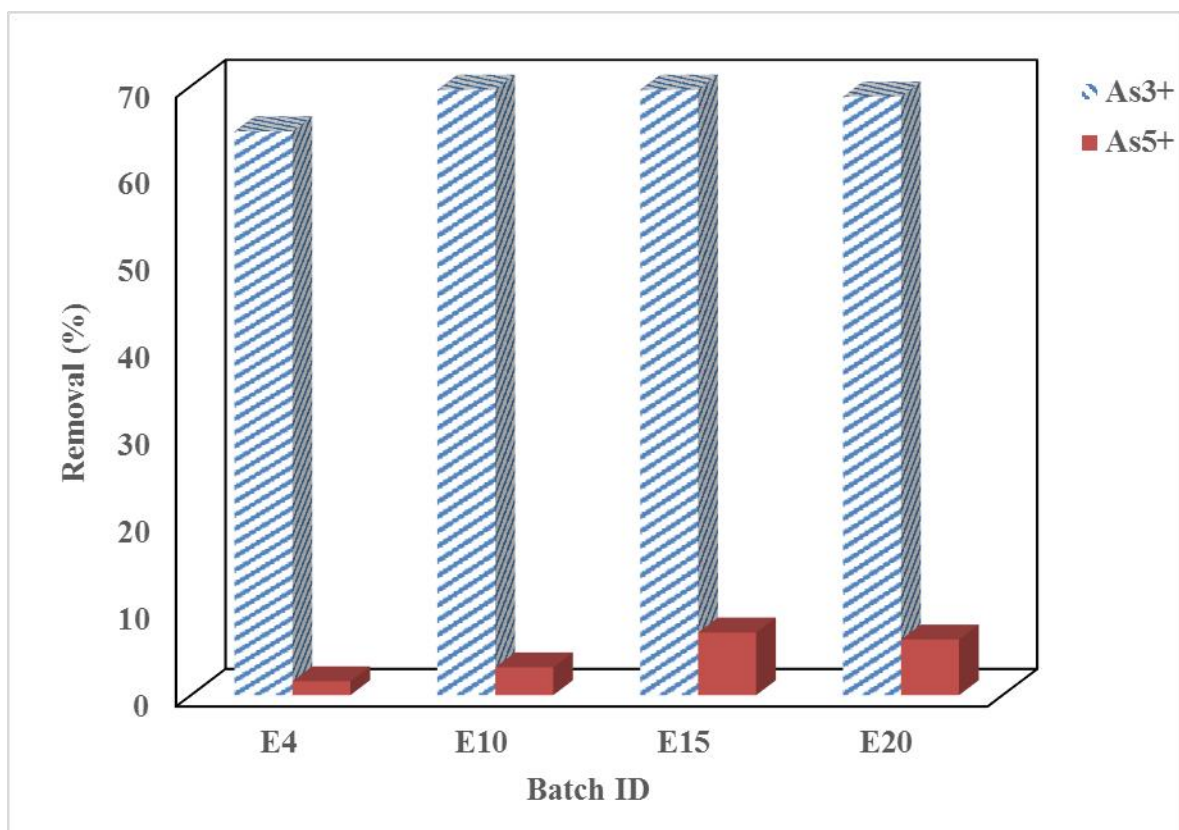
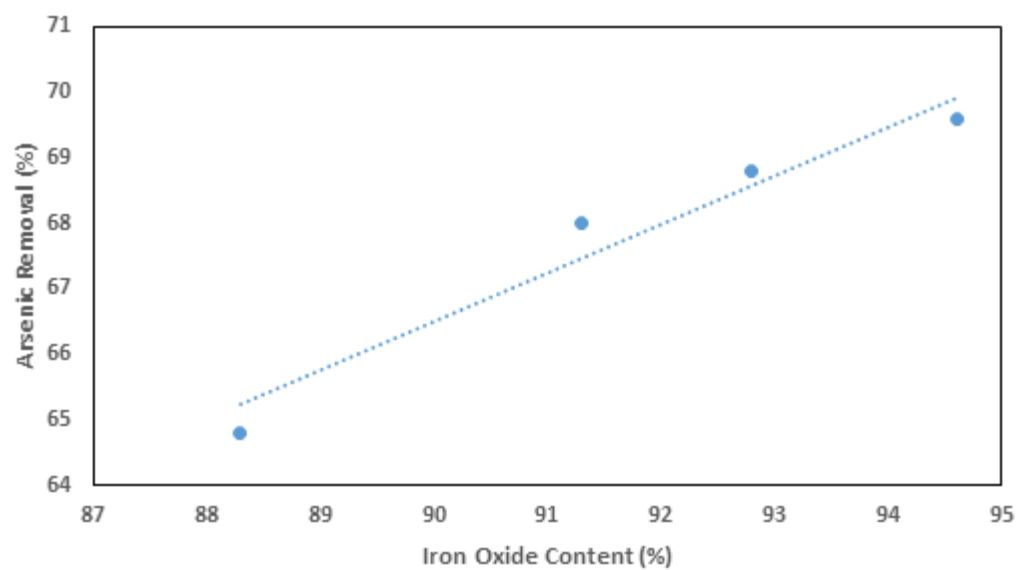


Figure 13: Comparison of removal efficiency of granules from different batches. The adsorbent granules from batches 4, 10, and 15 and 20 were contacted with 1000ppb solution of the arsenic solutions for 3 days. The concentration of the solution were measure at the end of the test to determine % removal of arsenic from the solution.

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2

3 Figure 14: correlation between iron oxide content in the granules and percentage removal of arsenic (III). The percentage of
4 arsenic (III) removed is plotted against the iron oxide content of the adsorbent granules.

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